



US006527981B1

(12) **United States Patent**
Tseng et al.(10) **Patent No.:** **US 6,527,981 B1**
(45) **Date of Patent:** **Mar. 4, 2003**(54) **AZOLE/AMINE OXIDE PRESERVATIVES**(75) Inventors: **Chuen-ing Tseng**, Lawrenceville, NJ
(US); **Leigh E. Walker**, Macungie, PA
(US)(73) Assignee: **Lonza Inc.**, Fair Lawn, NJ (US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.(21) Appl. No.: **09/578,015**(22) Filed: **May 24, 2000****Related U.S. Application Data**(60) Provisional application No. 60/135,562, filed on May 24,
1999.(51) **Int. Cl.⁷** **C09K 3/00**(52) **U.S. Cl.** **252/384; 428/541; 428/907;**
106/18.32(58) **Field of Search** 252/384; 428/541,
428/907; 106/18.32(56) **References Cited****U.S. PATENT DOCUMENTS**

3,296,145	A	1/1967	Findlan et al.	252/106
3,484,523	A	12/1969	Findlan et al.	424/248
3,658,985	A	* 4/1972	Olson	424/70
3,761,488	A	9/1973	Lewis et al.	260/302
4,005,193	A	1/1977	Green et al.	424/168
4,105,431	A	8/1978	Lewis et al.	71/67
4,379,810	A	4/1983	Amundsen et al.	428/541
4,382,105	A	5/1983	Amundsen et al.	427/370
4,526,699	A	7/1985	Jones et al.	252/99
4,622,248	A	11/1986	Leach et al.	427/440
4,857,322	A	8/1989	Goettsche et al.	424/633
4,888,349	A	* 12/1989	Brandes	514/383
4,929,454	A	5/1990	Findlay et al.	424/638
4,937,143	A	6/1990	West	427/419.8
4,950,685	A	8/1990	Ward	514/479
4,961,878	A	* 10/1990	Mullins	252/389.3
5,073,570	A	12/1991	Tseng	514/533
5,276,029	A	1/1994	Goettsche et al.	514/231.2
5,304,237	A	4/1994	Barth et al.	106/18.3
5,426,121	A	6/1995	Bell	514/500
5,468,284	A	11/1995	Sturm	106/2
5,486,315	A	1/1996	Tseng	252/547
5,500,153	A	3/1996	Figuroa et al.	252/548
5,527,384	A	6/1996	Williams et al.	106/18.32
5,536,505	A	7/1996	Yu	106/18.33
H1635	H	3/1997	Vander Meer	510/220
5,833,741	A	11/1998	Walker	106/2
5,858,921	A	1/1999	Magin et al.	504/206
5,891,836	A	4/1999	Kacher	510/237
5,922,672	A	7/1999	Stringer et al.	510/503
5,929,016	A	7/1999	Harrison	510/384
6,037,316	A	3/2000	Garner et al.	510/238
6,075,030	A	* 6/2000	Wagner	514/275
6,080,715	A	6/2000	Bianchi et al.	510/444
6,159,924	A	12/2000	Weller et al.	510/384
6,180,672	B1	1/2001	Lichtenberg et al.	514/561
6,395,698	B1	5/2002	Daun et al.	510/384
6,416,789	B1	7/2002	Marks et al.	424/641

FOREIGN PATENT DOCUMENTS

CA	1 174 005	9/1984	A01N/31/14
DE	3743 821 A1	7/1989	B27K/3/34
DE	4217 882 A1	12/1993	A01N/55/04
DE	44 41 674 A1	5/1996	C07C/275/32
DE	196 40 874	4/1998	B27K/3/34
DE	196 48 888 A1	5/1998	B27K/3/50
EP	0 370 182	5/1990	B27K/3/50
EP	0 381 482	8/1990	B27K/3/50
EP	0 571 846 A1	12/1993	A01N/47/12
JP	57022003	2/1982	B27K/3/52
JP	64-1796	1/1989	C11D/3/28
JP	1-268605	10/1989	A01N/33/24
JP	9059672	3/1997	
WO	97/01423	1/1997	B27K/3/50
WO	98/00008	1/1998	A01N/25/02
WO	98/18321	5/1998	A01N/25/30
WO	98/31518	7/1998	B27K/3/00
WO	WO-9833381 A1 *	8/1998	

OTHER PUBLICATIONSAmerican Wood Preservers' Association, P5-Waterborne
Preservatives, 4-5, 1998.Encyclopedia of Chemical Technology, vol 2, pp. 259-271,
John Wiley & Sons Inc., 1978.Archer et al., Forest Products Journal, 45(1):86-89, Jan.
1995.

Hirobumi et al., 120:301698 1993 (abstract).

Liu et al., 25th Annual Meeting of the International Research
Group on Wood Preservation, Nusa Dua Bali, Indonesia,
May 29, 1994-Jun. 3, 1994.Nicholas et al., 28th Annual Meeting of the International
Research Group on Wood Preservation, Whistler, Canada,
May 25, 1997-May 30, 1997.Williams et al., American Wood-Perservers' Association,
90:156-176, 1994.

* cited by examiner

Primary Examiner—Cephia D. Toomer(74) *Attorney, Agent, or Firm*—Darby & Darby(57) **ABSTRACT**

Applicants have discovered that amine oxides enhance the performance of azoles as fungicides and wood preservatives. Also, amine oxides have been found to provide waterproofing properties and enhance the uniform distribution and penetration of azoles into wood substrates. The present invention provides a composition comprising an amine oxide and an azole, such as a 1,2,4-triazole. The composition of the present invention may be incorporated into or be a wood preservative and waterproofing system, or agricultural product. Another embodiment of the present invention is a method for preserving and/or waterproofing a wood substrate by applying the composition to the wood substrate. Yet another embodiment is an article comprising a wood substrate and the composition of the present invention. The invention also provides a method of controlling fungi comprising applying an effective amount of the composition of the present invention to the fungi or the area on which the fungi grow.

34 Claims, No Drawings

AZOLE/AMINE OXIDE PRESERVATIVES

This application claims the benefit of U.S. Ser. No. 60/135,562, filed May 24, 1999.

FIELD OF THE INVENTION

This invention relates to compositions containing an azole and an amine oxide and their use as wood preservative and waterproofing compositions and as fungicides in agricultural products.

BACKGROUND OF THE INVENTION

Azoles are generally known to be effective as wood preservatives. Azole compounds are registered with the US Environmental Protection Agency (EPA) for use in wood protection treatment to buildings, forest products, finished wood products, log houses, wooden aquatic structures, wooden containers, and pressure treated forest products. Azoles are also used in industrial preservation applications and agriculture applications to protect plants, fruits, vegetables, cereal crops and sugar crops from fungal attack.

Azole compounds are lipophilic, due to their organic nature, and have good solubility in organic medium. However, they typically have poor solubility in aqueous solutions. According to "The Pesticide Manual, 11th Edition", C. D. S. Tomlin, editor, published by the British Crop Protection Council, UK (1997), the solubility of propiconazole in water is 100 ppm at 20° C., and that of tebuconazole in water is 36 ppm at 20° C. A number of wood preservation concentrates have recently been developed to circumvent the water solubility problem.

DE 19648888 describes water-thinned wood preservative concentrates containing at least 5% triazole fungicide in an aqueous benzalkonium halide solution, e.g., a 50% aqueous (C₁₂₋₁₄ alkyl)benzyltrimethyl ammonium chloride solution.

WO 98/18321 describes a microbicide microemulsion containing a solvating surfactant selected from alkoxyated castor oil, alkoxyated hydrogenated castor oil and an alkoxyated rosin.

WO 98/00008 describes a liquid pesticidal composition containing azole compounds in an organic solvent and as surfactants (a) a castor oil ethoxylate having 30–50 mole ethoxylate, (b) a branched C₈–C₁₈ alcohol ethoxylate having 5–10 mole ethoxylate, and (c) a tristyrene phenol ethoxylate having 8–30 mole ethoxylate or its phosphate or salt.

DE 4441672 describes wood preservative compositions containing a dimethylalkylamine, an aliphatic C₈–C₂₀ dicarboxylic acid, propylene glycol and a triazole compound.

There is a continuing need for improved azole wood preservative and waterproofing compositions and azole anti-fungal compositions.

SUMMARY OF THE INVENTION

Applicants have discovered that amine oxides enhance the performance of azoles as fungicides and wood preservatives. Also, amine oxides have been found to provide waterproofing properties and enhance the uniform distribution and penetration of azoles into wood substrates. The present invention provides a composition comprising an amine oxide and an azole, such as a 1,2,4-triazole. The composition of the present invention may be incorporated into or be a wood preservative and waterproofing system, or agricultural product.

Another embodiment of the present invention is a method for preserving and/or waterproofing a wood substrate by applying the composition to the wood substrate.

Yet another embodiment is an article comprising a wood substrate and the composition of the present invention.

The invention also provides a method of controlling fungi comprising applying an effective amount of the composition of the present invention to the fungi or the area on which the fungi grow.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a composition comprising an amine oxide and an azole. Surprisingly, the fungicidal activity of the azole/amine oxide composition is substantially greater than the sum of the fungicidal activities of the amine oxides and azole separately.

The amine oxide also enhances the uniform distribution and penetration of the azole into wood substrates and improves leach resistance. Furthermore, the azole compositions of the present invention have high water solubility and low volatility.

The compositions of the present invention are useful as wood preservatives for protecting wood from staining, discoloring, molding, rotting and losing its mechanical properties. Wood products which can be preserved with the composition include, but are not limited to, timber, lumber, railway tiles, telephone poles, fences, windows and doors, plywood, particle board, oriented-strained board, chipboard, joinery, bridges and wood products which are generally used in houses, building, construction and carpentry.

The compositions are also useful in textile fibers, e.g., cotton and wool natural fibers and polyamide and polyester synthetic fibers; coatings, e.g., oil paints, dispersion paint, lacquers, and finishing stains; and adhesives and other materials which are degradable by fungi. The compositions may also advantageously be applied in the cellulose and paper industry, in particular to protect pulpwood for paper manufacture from fungal attack.

Additionally, the compositions are useful for industrial preservation to protect products from microbiological attack or degradation, which reduces or destroys their economic value. Examples of such products include, but are not limited to, latexes, adhesives, cellulose products, metal working fluids, coatings, and paint compositions.

The compositions of the present invention are effective against a broad range of fungi. Examples of such fungi include, but are not limited to, Ascomycetes (e.g., *Venturia*, *Podospaera*, *Erysiphe*, *Monilinia*, *Uncinula*, *Aureobasidium*, *Sclerophoma*); Basidiomycetes (e.g., *Hemileia*, *Rhizoctonia*, *Puccinia*, *Coniophora*, *Serpula*, *Poria*, *Uromyces*, *Gloeophyllum*, *Lentinus*, *Coriolus*, *Irpex*); and fungi imperfecti (e.g., *Botrytis*, *Helminthosporium*, *Rhynchosporium*, *Fusarium*, *Septoria*, *Cercospora*, *Alternaria*, *Pyricularia*, *Penicillium*, *Geotrichum*).

The amine oxide may be a trialiphatic substituted amine oxide, an N-alkylated cyclic amine oxide, a dialkylpiperazine di-N-oxide, an alkyl-di-(poly(oxyalkylene))amine oxide, a dialkylbenzylamine oxide, a fatty amidopropyl dimethyl amine oxide, a diamine oxide; a triamine oxide, or any combination of any of the foregoing. Preferably, the amine oxide includes at least one C₈–C₁₈ alkyl moiety.

Preferred trialiphatic substituted amine oxides have the formula R¹R²R³N→O, where R¹ is a linear, branched, cyclic or any combination thereof C₈ to C₄₀ saturated or unsaturated group; and R² and R³ independently are linear, branched, or any combination thereof C₁ to C₄₀ saturated or unsaturated groups. R¹, R², and R³ independently may be

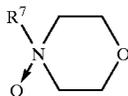
3

alkyl, alkenyl, or alkynyl groups. More preferably, R¹ is a linear, branched, cyclic or any combination thereof C₈ to C₂₂ saturated or unsaturated group, such as coco, hydrogenated tallow, soya, decyl, hexadecyl, and oleyl; and R² and R³ independently are linear, branched, or any combination thereof C₁ to C₂₂ saturated or unsaturated groups, such as coco, hydrogenated tallow, soya, decyl, and hexadecyl.

A preferred trialiphatic substituted amine oxide is a dialkylmethylamine oxide having the formula R¹R²CH₃N→O, where R¹ and R² are defined as above. Another preferred trialiphatic substituted amine oxide is an alkyl dimethylamine oxide having the formula R¹(CH₃)₂N→O, where R¹ is defined as above. More preferred alkyl dimethylamine oxides have the formula R¹⁹(CH₃)₂N→O, where R¹⁹ is a linear or branched C₈-C₁₈ alkyl or alkenyl. Preferably, R¹⁹ is a linear or branched C₈-C₁₆ alkyl. Alkyl dimethylamine oxides are non-toxic and non-mutagenic surfactants. Suitable alkyl dimethylamine oxides include, but are not limited to, a C₁₀ alkyl dimethylamine oxide, a C₁₀-C₁₄ alkyl dimethylamine oxide, a C₁₂-C₁₆ alkyl dimethylamine oxide, a C₁₆-C₁₈ alkyl dimethylamine oxide, and any combination of any of the foregoing.

Preferred N-alkylated cyclic amine oxides have the formula R⁴R⁵R⁶N→O where R⁴ is defined as R¹ above and R⁵ and R⁶ are linked to form a cyclic group. The cyclic group typically contains from 4 to 10 carbon atoms and may optionally contain oxygen, sulfur, nitrogen, or any combination of any of the foregoing. More preferred N-alkylated cyclic amine oxides include, but are not limited to, an alkylmorpholine N-oxide, a dialkylpiperazine di-N-oxide, and any combination of any of the foregoing.

Preferred alkylmorpholine N-oxides have the formula



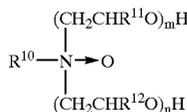
where R⁷ is defined as R¹ above. According to a more preferred embodiment, R⁷ is a linear or branched C₈ to C₁₆ alkyl. Examples of preferred alkylmorpholine N-oxides include, but are not limited to, cetyl morpholine N-oxide and lauryl morpholine N-oxide.

Preferred dialkylpiperazine di-N-oxides have the formula



where R⁸ is defined as R¹ above and R⁹ is defined as R² above.

Preferred alkyl di(poly(oxyalkylene))amine oxides have the formula



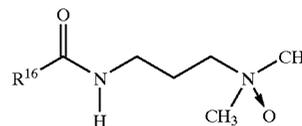
where R¹⁰ is defined as R¹ above; R¹¹ and R¹² independently are H or CH₃; and m and n independently are integers from about 1 to about 10.

Preferred dialkylbenzylamine oxides have the formula R¹³R¹⁴R¹⁵N→O, where R¹³ is defined as R¹ above; R¹⁴ is

4

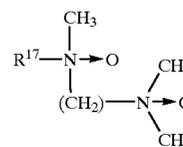
defined as R² above; and R¹⁵ is benzyl. More preferred dialkylbenzylamine oxides include, but are not limited to, alkylbenzylmethylamine oxides having the formula R¹³R¹⁵CH₃N→O where R¹³ and R¹⁵ are defined as above. According to a more preferred embodiment, R¹³ is a linear or branched C₈-C₁₂ alkyl.

Preferred fatty amidopropyl dimethyl amine oxides have the formula



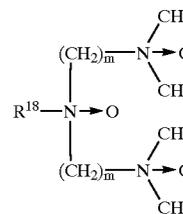
where R¹⁶ is defined as R¹ above.

Preferred diamine oxides have the formula



where R¹⁷ is defined as R¹ above; and m is an integer from about 1 to about 10.

Preferred triamine oxides have the formula



where R¹⁸ is defined as R¹ above; and m and n independently are integers from about 1 to about 10.

Long chain (C₁₆ or greater) amine oxides, such as hexadecylamine oxides and hydrogenated tallow amine oxides, are particularly preferable for imparting waterproofing properties to the composition. Short chain (C₁₄ and shorter) amine oxides aid in solubilizing the azole and long chain amine oxides.

The azole is preferably a 1,2,4-triazole. Suitable 1,2,4-triazoles include, but are not limited to, triadimefon, triadimenol, triazbutil, propiconazole, cyproconazole, difenoconazole, tebuconazole, myclobutanil, triadimenol, fenbuconazole, etaconazole, bromoconazole, flusiazole, uniconazole, diniconazole, bitertanol, hexaconazole, azaconazole, flutriafol, epoxiconazole, fluquinconazole, tetraconazole, penconazole, and any combination of any of the foregoing. Preferred azoles include, but are not limited to triadimefon, propiconazole, cyproconazole, tebuconazole, myclobutanil, fenbuconazole, and any combination of any of the foregoing. More preferably, the azole is propiconazole, tebuconazole, or any combination of any of the foregoing. The azole may also be a benzimidazole, such as thiabendazole, benomyl, and carbendazim.

A preferred amine oxide/azole combination is a C₁₀-C₁₆ alkyl dimethylamine oxide or a mixture of C₁₀-C₁₆ alkyl dimethylamine oxides with propiconazole, cyproconazole, tebuconazole, or a combination thereof. More preferred C₁₀-C₁₆ alkyl dimethylamine oxides for these combinations include, but are not limited to, coco-dimethylamine oxide, a

mixture of branched C₁₀-C₁₄ alkyl dimethyl amine oxides, and any combination of any of the foregoing.

The composition may include a solvent, such as water and water miscible solvents, including, but not limited to, alcohols, glycols, esters, ethers, polyethers, amides, and any combination of any of the foregoing.

The weight ratio of amine oxide to azole broadly ranges from about 5000:1 to about 0.1:1 and preferably ranges from about 100:1 to about 1:1. According to one preferred embodiment, the weight ratio ranges from about 40:1 to about 5:1 and is more preferably about 20:1.

According to one embodiment of the invention, the composition in concentrated form contains broadly from about 5 to about 100%, preferably from about 10 to about 50%, and more preferably from about 10 to about 35% by weight of combined amine oxide and azole based upon 100% weight of total composition.

Use dilutions of the composition typically comprise a fungicidally effective amount of azole and amine oxide. Generally, the use dilution comprises a fungicide enhancing effective amount of amine oxide, i.e., an amount of amine oxide sufficient to enhance the fungicidal efficacy of the azole. For wood applications, the use dilution may comprise a wood distribution, penetrating enhancing, waterproofing, and/or fungicide enhancing effective amount of amine oxide and a fungicidally effective amount of azole. Use dilutions preferably comprise from about 0.01 to about 5.0%, more preferably from about 0.1 to about 5.0%, and most preferably from about 0.5 to about 5.0% by weight of amine oxide, based upon 100% weight of total composition. Use dilutions preferably comprise from about 0.00001% (0.1 ppm) to about 2.0%, more preferably from about 0.0001% (1 ppm) to about 1.0%, and most preferably from about 0.0005% (5 ppm) to about 0.5% by weight of azole, based upon 100% weight of total composition.

The composition may be incorporated into or be a wood preservative and/or waterproofing system or an agricultural product.

Other adjuvants may be included in the composition as known to one of ordinary skill in the art. Examples of such adjuvants include, but are not limited to, thickeners, drying oils, anti-oxidants, UV absorbers, pigments, waxes, and any combination of any of the foregoing. Other biocides, fungicides and insecticides may be included in the composition. Any organic insecticide or fungicide that can be solubilized by an aqueous amine oxide solution is suitable for use in the present composition. Suitable insecticides include, but are not limited to, chloropyrifos, folpet, captafol, captan, pyrethroids, and any combination of any of the foregoing. Suitable fungicides include, but are not limited to, iodopropargyl butylcarbamate, tributyltin oxide, 2-(thiocyanomethylthio)benzothiazole, iodo-sulfones, azoles, isothiazalones, and any combination of any of the foregoing.

Another embodiment of the present invention is a method for preserving and/or waterproofing a wood substrate by applying the composition of the present invention to the wood substrate. The composition may be applied to the wood substrate by any method known to one of ordinary skill in the art. For example, the composition may be applied by treating the wood substrate under pressure or vacuum, in a thermal or dip system. Alternatively, it may be applied by a surface treatment, such as brushing, dipping, soaking, and spraying.

The invention also includes a method of controlling fungi comprising applying an effective amount of one or more compositions of the present invention. The term "control-

ling" as used herein includes, but is not limited to, inhibiting growth of fungi.

The composition of the present invention may be prepared by mixing the azole, amine oxide, solvents, and adjuvants. The mixture may be heated and/or stirred to expedite mixing.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate the invention without limitation. All parts and percentages are given by weight unless otherwise indicated.

The abbreviations "DMAO" and "BMAO" in the examples stand for dimethylamine oxide and benzyl methylamine oxide, respectively. The following ingredients were used in the examples:

- (a) branched alkyl (C₁₀-C₁₄) dimethylamine oxide (branched alkyl (C₁₀-C₁₄) DMAO), which is available as Barlox® 12i from Lonza Inc. of Fair Lawn, N.J.;
- (b) coco-alkyl (C₁₂-C₁₆) dimethylamine oxide (coco-DMAO) which is available as Barlox® 12 from Lonza Inc. of Fair Lawn, N.J.;
- (d) octyl dimethylamine oxide (octyl-DMAO), decyl dimethylamine oxide (decyl-DMAO), dodecyl dimethylamine oxide (dodecyl-DMAO), tetradecyl dimethylamine oxide (tetradecyl-DMAO), hexadecyl dimethylamine oxide (hexadecyl-DMAO), octadecyl dimethylamine oxide (octadecyl-DMAO), which are available as FMBAO-8™, Barlox® 10S, Barlox® 12S, Barlox® 14, Barlox® 16S, and Barlox® 18S, from Lonza Inc. of Fair Lawn, N.J.;
- (e) coco-alkyl-di(hydroxyethyl)amine oxide and tallow-alkyl-di(hydroxyethyl)amine oxide which are available as Aromox™ C/12 and Aromox™ T/12 from Akzo Chemical of Chicago, Ill.;
- (f) the other amine oxides described below can be prepared from the corresponding amine with hydrogen peroxide according to the procedure described in U.S. Pat. No. 5,486,315, which is herein incorporated by reference;
- (g) cyproconazole and propiconazole which are available from Janssen Pharmaceutica of Titusville, N.J.;
- (h) fenbuconazole and myclobutanil which are available from Rohm and Haas of Spring House, Pa.; and
- (i) tebuconazole and triadimefon which are available from Bayer Corporation of Pittsburgh, Pa.

Barlox® 100S, 12, 12i, 14, and 16S are 30% (w/w) aqueous solutions of their corresponding amine oxides. Barlox® 18S and FMBAO-8 are 25% and 40% (w/w) aqueous solutions of their corresponding amine oxides, respectively. Barlox® 10S, 12, 12i, and 14 and FMBAO-8 are liquids. Barlox® 16S and 18S are a viscous liquid and a paste, respectively.

EXAMPLE 1

1.06 g of propiconazole was dissolved in 16.88 g of 31.4% (w/w) coco-DMAO in water with stirring to form a solution containing about 29.5% by weight of coco-DMAO and about 5.89% by weight of propiconazole. The weight ratio of coco-DMAO to propiconazole was about 5:1.

3.39 g of the propiconazole/coco-DMAO solution having a weight ratio of about 5:1 was diluted with 96.61 g of water to form a clear solution containing about 1% by weight of coco-DMAO and about 0.05 g by weight of propiconazole.

0.45 g of propiconazole was dissolved in 28.66 g of 31.4% (w/w) coco-DMAO (in water) and 15.86 g of water with stirring to form a clear solution containing about 20% by weight of coco-DMAO and 1% by weight of propiconazole. The weight ratio of coco-DMAO to propiconazole was about 20:1.

5.00 g of the propiconazole/coco-DMAO solution having a weight ratio of about 20:1 was diluted with 95 g of water to form a clear solution containing about 1% by weight of coco-DMAO and about 0.05% by weight of propiconazole.

EXAMPLE 2

The procedure in Example 1 was repeated except that branched alkyl (C₁₀-C₁₄) DMAO was substituted for coco-DMAO.

EXAMPLE 3

1.06 g of tebuconazole was dissolved in 16.86 g of 31.4% (w/w) coco-DMAO in water with heating to from about 40 to about 50° C. and stirring to form a clear, colorless solution containing about 29.5% by weight of coco-DMAO and about 5.89% by weight of tebuconazole. The weight ratio of coco-DMAO to tebuconazole was about 5:1.

0.45 g of tebuconazole was dissolved in 28.66 g of 31.4% (w/w) coco-DMAO (in water) and 15.86 g of water with heating to from about 40 to about 50° C. and stirring to form a clear solution containing about 20% by weight of coco-DMAO and 1% by weight of tebuconazole. The weight ratio of coco-DMAO to tebuconazole was about 20:1. 5.00 g of the tebuconazole/coco-DMAO solution having a weight ratio of about 20:1 was diluted with 95 g of water to form a clear solution containing about 1% by weight of coco-DMAO and 0.05% by weight of tebuconazole.

EXAMPLE 4

The procedure in Example 3 was repeated except that triadimefon was substituted for tebuconazole.

EXAMPLE 5

20.0 g of dodecyl-DMAO in solid form (95% purity) was mixed well with 1.0 g of tebuconazole powder to obtain a solid white mixture.

1.05 g of the tebuconazole/dodecyl-DMAO mixture was added to 98.95 g of water to form a clear, colorless solution containing about 1% by weight of dodecyl-DMAO and about 0.05% by weight of tebuconazole.

EXAMPLE 6

The procedure in Example 1 was repeated with the azoles and amine oxides in the amounts specified in Table 1 below. The solubility of the azoles in the solution is shown in Table

TABLE 1

Solubility of Azoles in Amine Oxides				
Azole	Amine Oxide	% by weight of Azole	% by weight of Amine Oxide	Soluble
Cyproconazole	Coco-DMAO	5.00	28.50	Yes
Fenbuconazole		1.00	29.70	Yes
Myclobutanil		5.00	28.50	Yes
Propiconazole		5.00	28.50	Yes

TABLE 1-continued

Solubility of Azoles in Amine Oxides				
Azole	Amine Oxide	% by weight of Azole	% by weight of Amine Oxide	Soluble
Tebuconazole		3.00	29.10	Yes
Triadimefon		2.50	29.25	Yes
Cyproconazole	Branched Alkyl	5.00	28.50	Yes
Fenbuconazole	(C ₁₀ -C ₁₄)-DMAO	1.00	29.70	Yes
Myclobutanil		5.00	28.50	Yes
Propiconazole		5.00	28.50	Yes
Tebuconazole		3.00	29.10	Yes
Triadimefon		2.50	29.25	Yes
Cyproconazole	Decyl-DMAO	5.00	28.50	Yes
Fenbuconazole		1.00	29.70	Yes
Myclobutanil		5.00	28.50	Yes
Propiconazole		5.00	28.50	Yes
Tebuconazole		5.00	29.10	Yes
Triadimefon		2.50	29.63	Yes

COMPARATIVE EXAMPLE 6A

The solubility of propiconazole, tebuconazole, and triadimefon (without amine oxide) in water is shown in Table 2 below. "The Pesticide Manual, 11th Edition", C. D. S. Tomlin, editor, published by The British Crop Protection Council, UK (1997).

TABLE 2

Azole	Appearance	Solubility in water ^a	Solubility in Water ^b
Cyproconazole	White Powder	140 ppm/25° C.	140 ppm at 22° C.
Fenbuconazole	Off-White Powder	0.2 ppm/25° C.	4 ppm at 25° C.
Myclobutanil	Off-White Powder	142 ppm/25° C.	142 ppm at 25° C.
Propiconazole	Brown Oil	100 ppm/20° C.	100 ppm at 20° C.
Tebuconazole	White Powder	36 ppm/20° C.	32 ppm at 20° C.
Triadimefon	White Powder	64 ppm/20° C.	64 ppm at 20° C.

^a"The Pesticide Manual, 11th Edition", C.D.S. Tomlin, editor, published by The British Crop Protection Council, UK (1997).

^bMaterial Safety Data Sheet of respective azoles.

^cAlso found in Bayer Technical Information Sheet No. N-107, Bayer Corporation of Pittsburgh, PA.

COMPARATIVE EXAMPLE 6B

Aqueous mixtures containing 1% by weight of propiconazole and 20% by weight of 4-methyl morpholine-N-oxide, pyridine N-oxide, trimethylamine oxide, or dimethylbenzylamine oxide were prepared. The weight ratio of amine oxide to propiconazole in each solution was about 20:1. In all the solutions, the propiconazole was not soluble in the solution and oiled out at the bottom of the flask.

EXAMPLE 7

A composition solution containing 5.0% by weight of propiconazole and 95% by weight of Barlox® 12 was prepared. Barlox® 12 is an aqueous solution containing 30% by weight of coco-DMAO. This composition was stored at room temperature for 13 months. NMR spectroscopy was used to analyze the sample. No decomposition of the composition was observed.

A composition solution containing 5.0% by weight of tebuconazole and 95% by weight of Barlox® 12 was prepared. This composition was stored at room temperature for 1 year. No decomposition of the composition was observed.

EXAMPLE 8

The corrosivity of the aqueous azole/amine oxide solutions in Table 3 was determined as follows. Approximately 20 mL of each aqueous test solution was prepared containing 1% by weight of amine oxide and 0.05% by weight of azole. The test solution was added to a Wheaton borosilicate glass scintillation vial having a polyethylene screw cap. A $\frac{1}{2} \times 1\frac{1}{2} \times 0.032$ " low carbon steel coupon with a $\frac{1}{4}$ " hole

punched $\frac{1}{4}$ " from the top edge, available from Q-Panel Company of Cleveland, Ohio, was suspended from the cap via teflon coated clips. After suspension, the bottom edge of the coupon was approximately $\frac{1}{16}$ " to $\frac{3}{32}$ " above the bottom of the vial. The coupon was immersed in the solution and stored at room temperature. The coupon was observed for signs of corrosion after 24 hours, 2 weeks, and 24 days.

The results are shown in Table 3 below.

TABLE 3

Amine Oxide	Azole	Initial Solution	Observation after 24 Hours	Observation after 14 Days	Observation after 24 Days
Octyl-DMAO	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion
Decyl-DMAO	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion	Slight Edge Corrosion
Dodecyl-DMAO	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion
Branched Alkyl (C ₁₀ -C ₁₄) DMAO	Propiconazole	Clear, Colorless Solution	No Corrosion	Slight edge corrosion on coupon	Edge Corrosion
Coco-DMAO	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion
Hexadecyl-DMAO	Propiconazole	Clear, Colorless Solution	lightly turbid	No Corrosion	No Corrosion
Octadecyl-DMAO	Propiconazole	Turbid Solution	No Corrosion	No Corrosion	No Corrosion
Oleyl-DMAO	Propiconazole	Clear, light yellow Solution	No Corrosion	No Corrosion	No Corrosion
Dodecylbenzyl methylamine oxide	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion
Cetyl morpholine N-oxide	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion
Branched Alkyl (C ₁₀ -C ₁₄) DMAO	Tebuconazole	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion
Coco-DMAO	Tebuconazole	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion
Coco-DMAO	Triadimefon	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion

COMPARATIVE EXAMPLE 8A

The corrosivity of the solutions in Table 4 was determined by the procedure described in Example 8. The results are shown in Table 4 below.

TABLE 4

Solution	Initial Solution	Observation after 24 hours	Observation after 14 Days	Observation after 24 Days
De-ionized water	Clear, Colorless Solution	Coupon has black surface	Solution rusty and coupon rust colored	Solution rusty and coupon rust colored
1% by weight of NP-1 Sapstain Control Chemical ^{TM1}	Turbid	Rusty, Orange precipitation	Rusty, Orange precipitation	Rusty, Orange precipitation
1% by weight of didecylmethyl ammonium chloride ²	Clear, Colorless Solution	Black corrosion	Black precipitation, corrosion on coupon surface	Black precipitation, corrosion on coupon surface
1% by weight of	Blue, clear	Rust	Rust	Rust precipitation,

TABLE 4-continued

Solution	Initial Solution	Observation after 24 hours	Observation after 14 Days	Observation after 24 Days
ammoniated copper quat, type D ³	solution	precipitation	precipitation, corrosion on coupon edge	corrosion on coupon edge
1% by weight of alkyl (C ₁₂ -C ₁₆) benzyl dimethyl ammonium chloride ⁴	Clear, light yellow Solution	Coupon surface black	Coupon surface black, rust precipitation	Coupon surface black, rust precipitation
1% by weight of didecyl dimethyl ammonium carbonate ⁵	Clear, Colorless Solution	No Corrosion	No Corrosion	No Corrosion

¹NP-1 Sapstain Control Chemical™ is available from Kop-Coat Inc. of Pittsburgh, PA.

²Didecyl dimethyl ammonium chloride is available as Bardac 2280 from Lonza Inc.

³Ammoniated copper quat, type D, is available from Chemical Specialties, Inc. of Charlotte, NC. It is prepared following the procedure described in "American Wood-Preservers' Association Standard", published by American Wood Preservers Association, pages 12-13 (1999).

⁴Alkyl (C₁₂-C₁₆) benzyl dimethyl ammonium chloride is available as Barquat 80-28 from Lonza Inc.

⁵Didecyl dimethyl ammonium carbonate can be prepared according to the procedure described in WO 94/28715.

EXAMPLE 9

The corrosivity of the aqueous azole/amine oxide solutions in Table 5 on aluminum was determined as follows. Approximately 40 mL of each aqueous test solution was prepared containing 1% by weight of amine oxide and 0.05% by weight of azole. The test solution was added to a 8-dram borosilicate glass vial (25 mm outer diameter x 95 mm height, 32 mL) having a polyethylene screw cap. A 3" x 1/2" x 1/16" aluminum coupon with a 1/4" hole punched 1/4"

from the top edge and having a 120 grit surface, available from Metal Samples Co. of Munford, Ala., was suspended from the cap via teflon coated clips. After suspension, the bottom edge of the coupon was approximately 1/16" to 3/32" above the bottom of the vial. The coupon was immersed in the solution and stored at about 50° C. The coupon was observed for signs of corrosion after 2 weeks and 8 months.

The results are shown in Table 5 below.

TABLE 5

Amine Oxide	Azole	Initial Solution	Observation after 14 Days	Observation after 8 Months
Decyl-DMAO	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion
Branched alkyl (C ₁₀ -C ₁₄) DMAO	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion
Coco-DMAO	Propiconazole	Clear, Colorless Solution	No Corrosion	No Corrosion
Coco-DMAO	Tebuconazole	Clear, Colorless Solution	No Corrosion	No Corrosion
Coco-DMAO	Triadimefon	Clear, Colorless Solution	No Corrosion	No Corrosion
Hexadecyl-DMAO	Propiconazole	Homogeneous, Turbid Solution	No Corrosion	No Corrosion
Octadecyl-DMAO	Propiconazole	Homogeneous, Turbid Solution	No Corrosion	No Corrosion
Cetyl morpholine N-oxide	Propiconazole	Clear, Colorless Solution	No Corrosion	Solution Clear; Trace Sediments
Oleyl-DMAO	Propiconazole	Clear, Light Yellow Solution	No Corrosion	No Corrosion

COMPARATIVE EXAMPLE 9A

⁵⁵ The procedure described in Example 9 was repeated with the solutions in Table 8 below. These solutions did not contain any azoles. The results are also shown in Table 6.

TABLE 6

Solution	Initial Solution	Observation after 14 Days	Observation after 8 Months
De-ionized water	Clear, Colorless Solution	Coupon Corroding, No Sediments	Coupon Corroding, Trace Sediments
1% by weight of	Clear, Colorless	Solution With	Solution With

TABLE 6-continued

Solution	Initial Solution	Observation after 14 Days	Observation after 8 Months
didecyldimethyl ammonium chloride ¹	Solution	Sediments	Sediments
1% by weight of ammoniated copper quat, type D ²	Dark Blue & Clear Solution	Dark Blue and Clear Solution; Sediments; Coupon Corroding	Brown Coupon; White Sediment; Bad Corrosion
1% by weight of didecyldimethyl ammonium carbonate ³	Clear, Colorless Solution	Hazy Liquid; Lots of Sediment	Hazy Liquid; Lots of Sediment
1% by weight of alkyl (C ₁₂ -C ₁₆) benzylidimethyl ammonium chloride ⁴	Clear, Colorless Solution	No Corrosion	Clear Solution; Trace Sediments

¹Didecyldimethyl ammonium chloride is available as Bardac ® 2280 from Lonza Inc.

²Ammoniated copper quat, type D, is available from Chemical Specialties, Inc. of Charlotte, NC. It is prepared following the procedure described in "American Wood-Preservers' Association Standard", published by American Wood Preservers Association, pages 12-13 (1999).

³Didecyldimethyl ammonium carbonate is prepared according to the procedure described in WO 94/28715.

⁴Alkyl (C₁₂-C₁₆) benzylidimethyl ammonium chloride is available as Barquat ® 80-28 from Lonza Inc.

EXAMPLE 10

The efficacy of the aqueous amine oxide solutions in Table 7 at various concentrations against the wood rot fungi *T. versicolor* (white rot fungi), *G. trabeum* (brown rot fungi), *P. placenta* (brown rot fungi), and *C. globosum* (soft rot decay fungi) were determined using the agar dilution plate method well known in the art. The minimum concentration of each amine oxide required to achieve 100% growth

25 retardation of each specific organism, i.e., the minimum inhibitory concentration (MIC), was determined. The percent retardation of the fungi was determined by the percentage change in the diameter of the fungi on the agar plate (i.e. Percent Retardation=((Diameter of Control)-(Diameter of Treated Fungi))/(Diameter of Control)*100%).

The results are shown in Table 7 below.

TABLE 7

Amine Oxide	MIC (ppm of amine oxides)			
	<i>T. versicolor</i> (ppm)	<i>G. trabeum</i> (ppm)	<i>P. placenta</i> (ppm)	<i>C. globosum</i> (ppm)
Octyldimethylamine oxide	750	1000	1000	>1000
Decyl-DMAO	750	250	500	>1000
Coco-DMAO	750	500	500-1000	>1000
Branched alkyl (C ₁₀ -C ₁₄) DMAO	500	250	500	>1000
Dodecyl-DMAO	250	250	250	>1000
Tetradecyl-DMAO	>1000	>1000	>1000	>1000
Hexadecyl-DMAO	>1000	>1000	>1000	>1000
Oleyl-DMAO	>1000	>1000	>1000	>1000
Octadecyl-DMAO	>1000	>1000	>1000	>1000
Behenyl DMAO	>1000	>1000	>1000	>1000
Coco-di(hydroxyethyl)-amine oxide	500	500	500	>1000
Tallow-di(hydroxyethyl)-amine oxide	>1000	>1000	>1000	>1000
Dodecyl-BMAO	>1000	1000	>1000	>1000
Lauryl morpholine N-oxide	750	1000	500	>1000

15

The minimum concentration of the aqueous amine oxide solutions in Table 8 required to achieve 50% growth retardation of each specific organism, i.e., IC₅₀, was estimated from the data obtained using Table2D curve fitting. The results are shown in Table 8.

TABLE 8

Fungi	Barlox ® 12		Barlox ® 12i		Bardac ® 2280	
	IC ₅₀ (ppm)	MIC (ppm)	IC ₅₀ (ppm)	MIC (ppm)	IC ₅₀ (ppm)	MIC (ppm)
<i>T. versicolor</i>	51	750	84	500	28	>1000
<i>G. trabeum</i>	9	500	44	250	8	>1000
<i>P. placenta</i>	5	1000	89	500	<5	1000
<i>C. globosum</i>	47	>1000	153	>1000	28	>1000

Barlox ® 12 is an aqueous solution containing 30% by weight of coco-DMAO.

Barlox ® 12i is an aqueous solution containing 30% by weight of branched (C₁₀-C₁₄) alkyl-DMAO.

Bardac ® 2280 is an 80% (w/w) aqueous solution of didecyldimethyl ammonium chloride and is available as Bardac 2280 from Lonza Inc.

The IC₅₀ and MIC concentrations in Tables 7 and 8 above are in ppm of amine oxides and didecyldimethyl ammonium chloride.

16

EXAMPLE 11

The efficacy of the aqueous azole solutions in Table 9 at various concentrations against the wood rot fungi *T. versicolor* (white rot fungi), *G. trabeum* (brown rot fungi), *P. placenta* (brown rot fungi), and *C. globosum* (soft rot decay fungi) were determined using the agar dilution plate method well known in the art. The minimum concentration of each azole required to achieve 100% growth retardation of each specific organism, i.e., the minimum inhibitory concentration (MIC), was determined. The minimum concentration of each azole required to achieve 50% growth retardation of each specific organism, i.e., IC₅₀, was estimated from the data obtained using Table2D curve fitting. The percent retardation of the fungi was determined by the percentage change in the diameter of the fungi on the agar plate (i.e. Percent Retardation=((Diameter of Control)-(Diameter of Treated Fungi))/(Diameter of Control)*100%).

The results are shown in Table 9 below.

TABLE 9

Azole	<i>T. versicolor</i>		<i>G. trabeum</i>		<i>P. placenta</i>		<i>C. globosum</i>	
	IC ₅₀ (ppm)	MIC (ppm)						
Cyproconazole	0.2	2.5	0.3	2.5	0.7	2.5	2.3	25
Fenbuconazole	1.1	25	0.3	50	3.9	25	10.7	50
Myclobutanil	6	50	4.3	>50	13	50	—	>50
Propiconazole	3	50	0.9	>50	0.7	50	11.7	>50
Tebuconazole	2.3	25	<0.1	10	1.7	50	34.5	50-500

EXAMPLE 12

The efficacy of aqueous propiconazole/amine oxide solutions containing the amine oxides in Table 10 against the wood rot fungi *T. versicolor* (white rot fungi), *G. trabeum* (brown rot fungi), *P. placenta* (brown rot fungi), and *C. globosum* (soft rot decay fungi) were determined using the agar dilution plate method well known in the art. Each solution was tested at dilutions of 0.5, 5, 50, and 250 ppm of propiconazole. The weight ratio of amine oxide to azole was about 20:1 in each solution. The percent retardation of the fungi was determined by the percentage change in the diameter of the fungi on the agar plate (i.e. Percent Retardation=((Diameter of Control)-(Diameter of Treated Fungi))/(Diameter of Control)*100%).

60

65

The results are shown in Table 10 below.

TABLE 10

Amine Oxide	Concentration of Propiconazole (ppm)	Percent Retardation			
		<i>T. Versicolor</i>	<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. globosum</i>
Octyldimethylamine oxide	250	100	100	100	100
	50	100	100	100	100
	5	100	89	100	85
Decyl-DMAO	0.5	11	69	62	42
	250	100	100	100	100
	50	100	100	100	100
Dodecyl-DMAO	5	100	100	100	81
	0.5	19	69	71	46
	250	100	100	100	100
Branched alkyl (C ₁₀ -C ₁₄) DMAO	50	100	100	100	100
	5	100	100	100	100
	0.5	49	71	69	45
Coco-DMAO	250	100	100	100	100
	50	100	100	100	90
	5	100	100	100	84
Tetradecyl-DMAO	0.5	13	72	76	52
	250	100	100	100	84
	50	100	100	100	83
Hexadecyl-DMAO	5	87	86	100	80
	0.5	5	64	73	51
	250	100	100	100	86
Octadecyl-DMAO	50	100	100	100	85
	5	89	85	100	81
	0.5	15	68	81	51
Oleyl-DMAO	250	100	100	100	97
	50	100	100	100	89
	5	91	85	100	77
Behenyl-DMAO	0.5	16	61	60	48
	250	100	100	100	83
	50	100	86	100	83
Coco-di(hydroxyethyl) amine oxide	5	90	83	100	70
	0.5	50	59	63	31
	250	100	100	100	97
Tallow- di(hydroxyethyl)amine oxide	50	100	100	100	88
	5	86	85	100	73
	0.5	11	61	55	42
Cetyl morpholine N-oxide	250	100	100	100	100
	50	100	100	100	88
	5	100	86	100	71
Didodecyl methyl amine oxide	0.5	19	68	61	44
	250	100	100	100	87
	50	100	87	100	86
Dodecyl-BMAO	5	100	85	100	76
	0.5	28	67	65	51
	250	100	100	100	86
Lauryl morpholine N-oxide	50	100	100	100	84
	5	87	81	100	63
	0.5	16	62	69	4
Octyl-BMAO	250	100	100	100	100
	50	100	100	100	81
	5	94	84	100	71
Didecylmethyl ammonium chloride (Bardac ® 2280)	0.5	14	58	74	43
	250	100	100	100	97
	50	100	100	100	90
Didecylmethyl ammonium chloride (Bardac ® 2280)	5	88	82	100	71
	0.5	36	68	64	41
	250	100	100	100	100
Didecylmethyl ammonium chloride (Bardac ® 2280)	50	100	100	100	85
	5	100	84	100	66
	0.5	34	68	72	30
Didecylmethyl ammonium chloride (Bardac ® 2280)	250	100	100	100	97
	50	100	100	100	100
	5	100	100	100	88
Didecylmethyl ammonium chloride (Bardac ® 2280)	0.5	13	67	65	48
	250	100	100	100	100
	50	100	100	100	86
Didecylmethyl ammonium chloride (Bardac ® 2280)	5	100	82	100	80

TABLE 10-continued

Amine Oxide	Concentration of Propiconazole (ppm)	Percent Retardation			
		<i>T. Versicolor</i>	<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. globosum</i>
—	0.5	39	68	83	66
(Bardap ® 26)	250	100	100	100	100
	50	100	100	100	86
	5	100	76	100	83
	0.5	40	70	81	65

EXAMPLE 13

15

The procedure described in Example 12 was repeated with the aqueous tebuconazole/amine oxide solutions in Table 11.

The results are shown in Table 11 below.

TABLE 11

Amine Oxide	Concentration of Tebuconazole (ppm)	Percent Retardation			
		<i>T. Versicolor</i>	<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. globosum</i>
Octyldimethylamine oxide	250	100	100	100	100
	50	100	100	100	100
	5	100	100	100	56
	0.5	81	76	47	28
Decyl-DMAO	250	100	100	100	100
	50	100	100	100	100
	5	100	100	100	58
	0.5	81	82	57	22
Dodecyl DMAO	250	100	100	100	100
	50	100	100	100	83
	5	100	100	100	70
	0.5	67	84	71	15
Branched alkyl (C ₁₀ -C ₁₄) DMAO	250	100	100	100	100
	50	100	100	100	100
	5	100	100	100	74
	0.5	70	83	43	-7
Coco-DMAO	250	100	100	100	100
	50	100	100	100	79
	5	100	100	100	63
	0.5	62	86	72	23
Tetradecyl-DMAO	250	100	100	100	78
	50	100	100	100	76
	5	100	100	100	58
	0.5	20	81	72	29
Hexadecyl-DMAO	250	100	100	100	83
	50	100	100	100	81
	5	100	100	100	44
	0.5	65	85	72	33
Octadecyl-DMAO	250	100	100	100	100
	50	100	100	100	82
	5	100	100	100	3
	0.5	58	78	51	21
Oleyl-DMAO	250	100	100	100	79
	50	95	100	100	74
	5	88	100	100	51
	0.5	48	82	56	34
Behenyl-DMAO	250	100	100	100	100
	50	100	100	100	82
	5	100	100	100	-8
	0.5	58	82	47	-26
Tallow- di(hydroxyethyl)amine oxide	250	100	100	100	78
	50	100	100	100	78
	5	86	100	100	45
	0.5	46	85	70	25
Cetyl morpholine N-oxide	250	100	100	100	76
	50	100	100	100	74
	5	100	100	100	51
	0.5	71	83	69	10
Dodecyl-BMAO	250	100	100	100	77

TABLE 11-continued

Amine Oxide	Concentration of Tebuconazole (ppm)	Percent Retardation			
		<i>T. Versicolor</i>	<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. globosum</i>
	50	100	100	100	76
	5	93	100	100	56
	0.5	56	84	68	21
Lauryl morpholine N-oxide	250	100	100	100	100
	50	100	100	100	82
	5	100	100	100	57
Octyl-BMAO	0.5	65	84	73	8
	250	100	100	100	100
	50	100	100	100	100
	5	95	100	100	53
	0.5	17	79	54	1

EXAMPLE 14

The procedure described in Example 12 was repeated with the aqueous cyproconazole/amine oxide solutions in Table 12.

The results are shown in Table 12 below.

TABLE 12

Amine Oxide	Concentration of Cyproconazole (ppm)	Percent Retardation			
		<i>T. Versicolor</i>	<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. globosum</i>
Coco-DMAO	50	100	100	100	100
	25	100	100	100	100
	5	100	100	100	74
	0.5	26	73	24	17

EXAMPLE 15

The procedure described in Example 12 was repeated with the aqueous fenbuconazole/amine oxide solutions in Table 13.

The results are shown in Table 13 below.

TABLE 13

Amine Oxide	Concentration of Fenbuconazole (ppm)	Percent Retardation			
		<i>T. Versicolor</i>	<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. globosum</i>
Coco-DMAO	100	100	100	100	100
	50	100	100	100	100
	5	100	100	100	73
	0.5	49	77	65	40

EXAMPLE 16

The procedure described in Example 11 was repeated with the aqueous myclobutanil/amine oxide solutions in Table 14. The results are shown in Table 16 below.

TABLE 14

Amine Oxide	Concentration of Myclobutanil (ppm)	Percent Retardation			
		<i>T. Versicolor</i>	<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. globosum</i>
Coco-DMAO	100	100	100	100	86
	50	100	100	100	84
	5	100	100	100	64
	0.5	75	74	62	26

EXAMPLE 17

The procedure described in Example 11 was repeated with the aqueous triadimefon/amine oxide solutions in Table 15. The results are shown in Table 15 below.

TABLE 15

Amine Oxide	Concentration of Triadimefon (ppm)	Percent Retardation			
		<i>T. Versicolor</i>	<i>G. trabeum</i>	<i>P. placenta</i>	<i>C. globosum</i>
Octyl-DMAO	250	100	100	100	100
	50	100	100	100	80
	5	90	86	100	56
	0.5	21	73	45	17
Coco-DMAO	250	100	100	100	88
	50	100	100	100	75
	5	100	100	100	53
	0.5	21	76	59	16
Branched alkyl (C ₁₀ -C ₁₄) DMAO	250	100	100	100	100
	50	100	100	100	100
Hexadecyl-DMAO	5	100	100	100	40
	0.5	18	62	36	-17
	250	100	100	100	77
	50	100	100	100	69
Cetyl morpholine N-oxide	5	89	85	100	56
	0.5	20	71	71	41
	250	100	100	100	72
	50	100	100	100	69
	5	100	87	100	36
	0.5	15	57	54	13

EXAMPLE 18

Synergism for the aqueous propiconazole/amine oxide solutions in Table 16 against *T. Versicolor* and *G. trabeum* were calculated by the methods described in C. E. Kull et al., "Mixtures of Quaternary Ammonium Compounds and Long-chain Fatty Acids as Antifungal Agents", *Applied Microbiology*, 9:538-541 (1961). The synergism value ($Q_A/Q_a + Q_B/Q_b$) was determined. Q_A is the concentration of amine oxide (in ppm) in an amine oxide/azole mixture, which yielded 100% retardation of a specific wood rot organism. Q_a is the concentration of amine oxide alone (in ppm) required to yield 100% retardation of a specific wood rot organism. Q_B is the concentration of azole (in ppm) in an amine oxide/azole mixture, which yielded 100% retardation of a specific wood rot organism. Q_b is the concentration of azole alone (in ppm) required to yield 100% retardation of a specific wood rot organism. All of the amine oxide/azole solutions in Table 19 exhibited 100% retardation of the specified wood rot organism.

When the value of ($Q_A/Q_a + Q_B/Q_b$) is less than one, the mixture is synergistic. Values for ($Q_A/Q_a + Q_B/Q_b$) of 1 and greater than 1, represent an additive effect and an antagonistic effect, respectively.

25

Q_a for coco-DMAO, decyl-DMAO, branched alkyl (C_{10} - C_{14})-DMAO, and dodecyl-DMAO against *T. versicolor* were determined to be 750, 750, 500, and 250 ppm, respectively. Q_a for coco-DMAO, decyl-DMAO, branched alkyl (C_{10} - C_{14})-DMAO, and dodecyl-DMAO against *G.*

26

Trabeum were determined to be 500, 250, 250, and 250 ppm, respectively. Q_a for decyl-DMAO, branched alkyl (C_{10} - C_{14})-DMAO, and dodecyl-DMAO against *P. placenta* were determined to be 500, 500, and 250 ppm, respectively. Q_b for propiconazole against *T. versicolor*, *G. trabeum*, and *P. placenta* were all determined to be 50 ppm.

TABLE 16

Amine Oxide	Concentration of Amine Oxide (ppm)	Concentration of Propiconazole (ppm)	$Q_A/Q_a + Q_B/Q_b$ (for <i>T. versicolor</i>)	$Q_A/Q_a + Q_B/Q_b$ (for <i>G. trabeum</i>)	
Coco-DMAO	250	2.5	0.38	0.55	
	250	0.5	0.34	0.51	
	200	5	0.37	0.50	
	200	1	0.29	0.42	
	125	5	0.27	0.35	
	125	2.5	0.22	0.30	
	50	10	0.27	0.30	
	50	0.5	0.08	0.11	
	25	10	0.23	0.25	
	25	5	0.13	0.15	
	25	2.5	0.08	0.10	
	12.5	2.5	0.07	0.08	
	10	25	0.51	0.52	
	5	25	0.51	0.51	
	Decyl-DMAO	100	5	0.23	0.5
	Branched Alkyl (C_{10} - C_{14})-DMAO	100	5	0.30	0.5
Dodecyl-DMAO	100	5	0.50	0.5	

30

The aqueous propiconazole/amine oxide solutions in Table 17 below were tested against *P. placenta*. The results are shown in Table 17 below.

35

TABLE 17

Amine Oxide	Concentration of Amine Oxide (ppm)	Concentration of Propiconazole (ppm)	$Q_A/Q_a + Q_B/Q_b$ (for <i>P. Placenta</i>)
Decyl-DMAO	100	5	0.3
Branched Alkyl (C_{10} - C_{14})-DMAO	100	5	0.3
Dodecyl-DMAO	100	5	0.5

45

EXAMPLE 19

The procedure described in Example 18 was repeated for the aqueous tebuconazole/amine oxide solutions in Tables 18 and 19. The results are shown in Tables 18 and 19.

Q_a for coco-DMAO, branched alkyl (C_{10} - C_{14})-DMAO, decyl-DMAO, dodecyl-DMAO, tetradecyl-DMAO, hexadecyl-DMAO, octadecyl-DMAO, behenyl-DMAO, octyl-DMAO, and lauryl morpholine N-oxide against *T. versicolor* were determined to be 750, 500, 750, 250, 1000, 1000, 1000, 750, and 750. Q_a for coco-DMAO, branched alkyl (C_{10} - C_{14})-DMAO, decyl-DMAO, and dodecyl-DMAO against *G. trabeum* were determined to be 500, 250, 250, and 250 ppm, respectively and Q_a for tetradecyl-DMAO, hexadecyl-DMAO, octadecyl-DMAO, behenyl-DMAO, octyl-DMAO, and lauryl morpholine N-oxide were all determined to be 1000 ppm. Q_a for decyl-DMAO, dodecyl-DMAO, and lauryl morpholine N-oxide against *P. placenta* were determined to be 500, 250, and 500 ppm, respectively, and Q_a for tetradecyl-DMAO, hexadecyl-DMAO, octadecyl-DMAO, behenyl-DMAO, and octyl-DMAO were all determined to be 1000 ppm. Q_b for tebuconazole against *T. versicolor*, *G. trabeum*, and *P. placenta* were determined to be 25, 10, and 50 ppm, respectively.

TABLE 18

Amine Oxide	Concentration of Amine Oxide (ppm)	Concentration of Tebuconazole (ppm)	Q _A /Q _a + Q _B /Q _b (for <i>T. vesicolor</i>)	Q _A /Q _a + Q _B /Q _b (for <i>G. trabeum</i>)	
Coco-DMAO	500	0.1	0.67	1.01	
	200	1	0.31	0.50	
	125	5	0.37	0.75	
	100	5	0.33	0.70	
	100	1	0.17	0.30	
	10	10	0.41	1.02	
	5	5	0.21	0.51	
	0.5	5	0.20	0.50	
	Branched Alkyl (C ₁₀ -C ₁₄)-DMAO	250	0.25	0.51	1.03
		125	5	0.45	1.00
100		5	0.40	0.90	
100		1	0.24	0.50	
25		1	0.09	0.20	
10		10	0.42	1.04	
5		5	0.21	0.52	
Decyl-DMAO	100	5	0.33	0.9	
	100	5	0.60	0.9	
Dodecyl-DMAO	100	5	0.30	0.6	
Tetradecyl-DMAO	100	5	0.30	0.6	
Hexadecyl-DMAO	100	5	0.30	0.6	
Octadecyl-DMAO	100	5	0.30	0.6	
Behenyl-DMAO	100	5	0.30	0.6	
Octyl-DMAO	100	5	0.33	0.6	
Lauryl morpholine N-oxide	100	5	0.33	0.6	

The aqueous solutions in Table 19 below were tested against *P. placenta*. The results are shown in Table 19 below.

TABLE 19

Amine Oxide	Concentration of Amine Oxide (ppm)	Concentration of Tebuconazole (ppm)	Q _A /Q _a + Q _B /Q _b (for <i>P. Placenta</i>)
Decyl-DMAO	100	5	0.3
Dodecyl-DMAO	100	5	0.5
Tetradecyl-DMAO	100	5	0.2
Hexadecyl-DMAO	100	5	0.2
Octadecyl-DMAO	100	5	0.2
Behenyl-DMAO	100	5	0.2
Octyl-DMAO	100	5	0.2
Lauryl morpholine N-oxide	100	5	0.3

EXAMPLE 20

The efficacy of the aqueous azole/amine oxide solutions in Table 20 were tested by the procedure described in Example 12. All of these compositions exhibited 100% retardation of *T. versicolor*, *G. trabeum*, and *P. placenta*.

TABLE 20

Amine Oxide	Azole	Concentration of Amine Oxide (ppm)	Concentration of Azole (ppm)
Coco-DMAO	Triadimefon	100	5
Branched Alkyl (C ₁₀ -C ₁₄)-DMAO	Triadimefon	100	5

TABLE 20-continued

Amine Oxide	Azole	Concentration of Amine Oxide (ppm)	Concentration of Azole (ppm)
Cetyl morpholine N-oxide	Tebuconazole	100	5
Octylbenzylmethyl amine oxide	Propiconazole	100	5

EXAMPLE 21

The waterproofing efficacy of the azole/amine oxide solutions in Table 21 on ponderosa pine end-grain wafers (5"×0.75"×0.25") was determined as follows. The sample wafers were equilibrated at ambient conditions before treating and were weighed. The samples were then placed in a vacuum desiccator equipped with an addition funnel and evacuated to a pressure (vacuum) of 0.1 atmosphere for 15 minutes. The treating solution was added to the sample and the pressure in the desiccator increased to atmospheric. The samples were allowed to remain in the solution for five minutes, then removed, blotted, and allowed to air dry to constant weight.

The samples were weighed and immersed in deionized water for about 30 minutes. The samples were removed, surface water was blotted and the samples were weighed and the weight percent of water absorbed was calculated for each sample.

Waterproofing ability is judged by the amount of water that is absorbed by a wooden specimen on immersion for a given time in water. Waterproofing index numbers (WR Index) were calculated by comparing a treated sample with

29

a matched untreated control specimen using the following equation:

$$\text{WR Index} = \frac{[\% \text{ Uptake Untreated Control} - \% \text{ Uptake Treated Sample}]}{\% \text{ Uptake Untreated Control}} \times 100$$

positive index number indicates a degree of waterproofing for the composition. Higher numbers are better than low numbers. A formulation that totally prevents water absorption would have a rating of 100. For certain millwork applications, an index of 60 is required.

The results are shown in Table 21 below.

TABLE 21

No.	Amine Oxide	Azole	Weight Ratio of Amine Oxide to Azole	% Water Uptake	WR Index
1	Coco-DMAO	Propiconazole	20	26.65	56
2	Branched alkyl (C ₁₀ -C ₁₃) DMAO	Propiconazole	20	28.64	53
3	Tetradecyl-DMAO	Propiconazole	20	31.70	48
4	Hexadecyl-DMAO	Propiconazole	20	14.49	76
5*	Octadecyl-DMAO	Propiconazole	20	14.68	76
6*	Behenyl-DMAO	Propiconazole	20	13.09	79
7	Dodecylbenzylmethyl amine oxide	Propiconazole	20	34.81	43
8	Tallow-di(hydroxyethyl) amine oxide	Propiconazole	20	15.97	74
9	Didecyl dimethyl ammonium chloride (control)	Propiconazole	20	39.22	36
10	Cetyl morpholine N-oxide	Propiconazole	20	26.41	57
11	Oleyl-DMAO	Propiconazole	20	31.15	49
12*	Didecylmethyl amine oxide	Propiconazole	20	21.76	64
13	Hexadecyl-DMAO	Tebuconazole	20	16.16	74
14*	Octadecyl-DMAO	Tebuconazole	20	16.91	72
15*	Behenyl-DMAO	Tebuconazole	20	11.92	80
16	Tallow-di(hydroxyethyl) amine oxide	Tebuconazole	20	17.14	72
17	Cetyl morpholine N-oxide	Tebuconazole	20	24.25	60
18	Oleyl-DMAO	Tebuconazole	20	31.62	48
19	Hexadecyl-DMAO	Triadimefon	20	17.59	71
20*	Octadecyl-DMAO	Triadimefon	20	17.81	71
21	Cetyl morpholine N-oxide	Triadimefon	20	17.09	72
22*	Didodecylpiperazine di-N-oxide	Triadimefon	20	23.99	61
23	Deionized Water (Control)	None	N/A	61.00	N/A

*The solution is milky.

45

All patents, applications, articles, publications, and test methods mentioned above are hereby incorporated by reference.

Many variations of the present invention will suggest themselves to those skilled in the art in light of the above detailed description. Such obvious variations are within the full intended scope of the appended claims.

What is claimed is:

1. A composition comprising a synergistic mixture of:

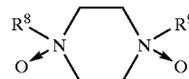
(a) a fungicide enhancing effective amount of one or more amine oxides selected from a group consisting of:

(i) a trialiphatic substituted amine oxide having the formula $R^1R^2R^3N \rightarrow O$, wherein R^1 is a linear or branched C₈ to C₂₂ saturated or unsaturated group; and R^2 and R^3 are independently linear or branched saturated or unsaturated C₈-C₂₂ groups;

(ii) an N-alkylated cyclic amine oxide having the formula $R^4R^5R^6N \rightarrow O$, wherein R^4 is a linear or branched C₈-C₄₀ saturated or unsaturated group and R^5 and R^6 are linked to form a cyclic group;

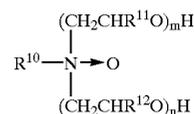
30

(iii) a dialkylpiperazine di-N-Oxide having the formula



wherein R^8 is a linear or branched C₈ to C₄₀ saturated or unsaturated group; and R^9 is a C₁ group, linear saturated or unsaturated C₂-C₄₀ group, or branched saturated or unsaturated C₃-C₄₀ group;

(iv) an alkyldi(poly(oxyalkylene))amine oxide having the formula

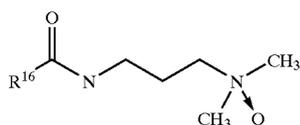


wherein R^{10} is a linear or branched C₈ to C₄₀ saturated or unsaturated group; R^{11} and R^{12} independently are H or CH₃; and m and n independently are integers from about 1 to about 10;

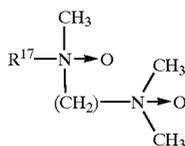
(v) a dialkylbenzylamine oxide having the formula $R^{13}R^{14}R^{15}N \rightarrow O$, wherein R^{13} is a linear or branched C₈ to C₄₀ saturated or unsaturated group; R^{14} is a C₁ group, linear saturated or unsaturated C₂-C₄₀ group, or branched saturated or unsaturated C₃-C₄₀ group; and R^{15} is benzyl;

(vi) a fatty amidopropyl dimethyl amine oxide having the formula;

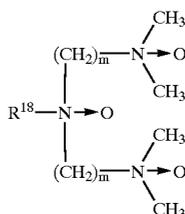
31



wherein R^{16} is a linear, branched or cyclic C_8 to C_{40} saturated or unsaturated group;
 (vii) a diamine oxide having the formula



wherein R^{17} is a linear or branched C_8 to C_{40} saturated or unsaturated group; and m is an integer from about 1 to about 10;
 (viii) a triamine oxide having the formula



wherein R^{18} is a linear or branched C_8 to C_{40} saturated or unsaturated group; and m and n independently are integers from about 1 to about 10; and
 (ix) any combination of the foregoing; and

(b) a fungicidal effective amount of one or more 1,2,4-triazoles or benzimidazoles.

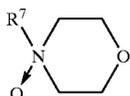
2. A composition as defined in claim 1, wherein R^4 is a linear or branched C_8 - C_{22} saturated or unsaturated group.

3. A composition as defined in claim 1, wherein the cyclic group of the N-alkylated cyclic amine oxide contains from 4 to 10 carbon atoms.

4. A composition as defined in claim 1, wherein the ring of the cyclic group of the N-alkylated cyclic amine oxide contains oxygen, sulfur, nitrogen, or any combination of any of the foregoing.

5. A composition as defined in claim 1, wherein said N-alkylated cyclic amine oxide is selected from the group consisting of an alkylmorpholine N-oxide, a dialkylpiperazine di-N-oxide, and any combination of any of the foregoing.

6. A composition as defined in claim 5, wherein said alkylmorpholine N-oxide has the formula



wherein R^7 is a linear or branched C_8 to C_{40} saturated or unsaturated group.

7. A composition as defined in claim 6, wherein R^7 is a linear or branched C_8 to C_{22} saturated or unsaturated group.

8. A composition as defined in claim 7, wherein R^7 is a linear or branched C_{10} to C_{16} alkyl.

32

9. A composition as defined in claim 1, wherein R^8 is a C_1 group, linear saturated or unsaturated C_2 - C_{22} group, or branched saturated or unsaturated C_3 - C_{22} group.

10. A composition as defined in claim 1, wherein R^{10} is a linear or branched C_8 to C_{22} saturated or unsaturated group.

11. A composition as defined in claim 1, wherein R^{13} is a linear or branched C_8 to C_{22} saturated or unsaturated group; and R^{14} is a C_1 group, linear saturated or unsaturated C_2 - C_{22} group, or branched saturated or unsaturated C_3 - C_{22} group.

12. A composition as defined in claim 1, wherein said dialkylbenzylamine oxide is an alkylbenzylmethylamine oxide having the formula $R^{13}R^{15}CH_3N \rightarrow O$, wherein R^{13} is a linear or branched C_8 to C_{40} saturated or unsaturated group; and R^{15} is benzyl.

13. A composition as defined in claim 1, wherein R^{13} is a linear or branched C_8 to C_{22} saturated or unsaturated group.

14. A composition as defined in claim 13, wherein R^{13} is a linear or branched C_8 to C_{12} saturated or unsaturated group.

15. A composition as defined in claim 1, wherein R^{16} is a linear, branched, cyclic or any combination thereof C_8 to C_{22} saturated or unsaturated group.

16. A composition as defined in claim 1, wherein R^{17} is a linear or branched C_8 to C_{22} saturated or unsaturated group.

17. A composition as defined in claim 1, wherein R^{18} is a linear or branched C_8 to C_{22} saturated or unsaturated group.

18. A composition as defined in claim 1, wherein said 1,2,4-triazole is selected from the group consisting of triadimefon, triazbutil, propiconazole, cyproconazole, difenoconazole, fluquinconazole, tebuconazole, myclobutanil, triadimenol, fenbuconazole, etaconazole, bromoconazole, flusiazole, uniconazole, diniconazole, bitertanol, hexaconazole, azaconazole, flutriafol, epoxiconazole, tetraconazole, penconazole, and any combination of any of the foregoing.

19. A composition as defined in claim 18, wherein said 1,2,4-triazole is selected from the group consisting of triadimefon, propiconazole, cyproconazole, tebuconazole, myclobutanil, fenbuconazole, and any combination of any of the foregoing.

20. A composition as defined in claim 18, wherein said 1,2,4-triazole is propiconazole.

21. A composition as defined in claim 18, wherein said 1,2,4-triazole is tebuconazole.

22. A composition as defined in claim 1, wherein said benzimidazole is selected from the group consisting of thiabendazole, benomyl, and carbendazim.

23. A composition as defined in claim 1, further comprising a solvent.

24. A composition as defined in claim 23, wherein said solvent is water.

25. A composition as defined in claim 23, wherein said solvent is selected from the group consisting of alcohols, glycols, esters, ethers, polyethers, and any combination of the foregoing.

26. A composition as defined in claim 1, wherein the weight ratio of said amine oxide to said azole ranges from about 100:1 to about 1:1.

27. A composition as defined in claim 26, wherein said weight ratio ranges from about 50:1 to about 5:1.

28. A composition as defined in claim 1, wherein said composition comprises from about 0.1 to about 5% by weight of amine oxide and from about 0.005 to about 0.5% by weight of azole based upon 100% weight of total composition.

33

29. An article comprising

(A) wood substrate; and

(B) a composition as defined in claim 1.

30. A method of controlling fungi comprising applying an effective amount of one or more compositions of claim 1 to the fungi on an area on which the fungi grow.

31. A composition comprising a synergistic mixture of:

(a) a fungicide enhancing effective amount of one or more trialiphatic substituted amine oxides having the formula $R^1R^2CH_3N\rightarrow O$, wherein R^1 is a linear or branched C_8 to C_{22} saturated or unsaturated group; and R^2 is a C^1 group, a linear saturated or unsaturated C_2 - C_{22} group, or branched saturated or unsaturated C_3 - C_{22} group;

(b) a fungicidal effective amount of one or more 1,2,4-triazoles selected from the group consisting of triadimefon, triazbutil, propiconazole, cyproconazole, difenoconazole, fluquinconazole, tebuconazole, myclobutanil, triadimenol, fenbuconazole,

34

etaconazole, bromuconazole, flusilazole, uniconazole, diniconazole, bitertanol, hexaconazole, azaconazole, flutriafol, epoxiconazole, tetraconazole, penconazole, and any combination of any of the foregoing,

wherein the weight ratio of amine oxide to 1,2,4-triazole ranges from about 100:1 to about 1:1.

32. A composition as defined in claim 31, wherein said trialiphatic substituted amine oxide is an alkyldimethylamine oxide having the formula $R^1(CH_3)_2N\rightarrow O$.

33. A composition as defined in claim 32, wherein R^1 is a linear or branched C_8 - C_{18} saturated or unsaturated group.

34. A composition as defined in claim 33, wherein said alkyldimethylamine oxide is selected from the group consisting of a C_{10} alkyldimethylamine oxide, a mixture of C_{10} - C_{14} alkyldimethylamine oxide, a mixture of C_{16} - C_{18} alkyldimethylamine oxide, and combination of any of the foregoing.

* * * * *